

THERMODYNAMIC SIMILARITY AND PREDICTION OF THE PROPERTIES
AND CHARACTERISTICS OF SUBSTANCES AND PROCESSES

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Principles of the theory of thermodynamic similarity are considered in application to all aggregate states of a substance, including phase transitions, and to the change in dissipative structures in open systems.

In truth it is now impossible to name any branch of natural science in which representations of the similarity of phenomena would not be utilized to some degree. But similarity reasoning reached its greatest development in the analysis of transformations of different kinds of energy, in particular, in modern thermodynamics that studies the equilibrium state of bodies and the nonequilibrium processes occurring therein.

Although the terminology "thermodynamic similarity" was introduced not so long ago (it was first formulated clearly in [1]), representations of the similarity of the properties of substances have a long history going back to Van der Waals and his known law of corresponding states. This law was established for the liquid and gaseous states of a substance, and the known Van der Waals equation of state for gases and liquids was its theoretical basis. It soon became clear that the law of corresponding states in its original form is not completely accurate, and consequently, is of limited value. In this connection, a more detailed examination was needed of those factors that actually govern the similarity of the properties of gaseous and liquid bodies. Meanwhile, it would be necessary to clarify whether similarity considerations could be extended to solid crystalline bodies and, if there is a foundation for this, to set up the corresponding characteristic similarity conditions. In particular the question of the similarity of melting curves that separate the crystalline and liquid phase domains required an answer. Furthermore, in connection with the discovery of several dissipative structures in open systems, that go over into each other under definite conditions, the important problem of the similarity of these transitions also occurred. The set of these as well as of other complex problems was the hypothesis for the recent creation of the theory of thermodynamic similarity in whose development Soviet scientists have contributed greatly. It is difficult to overestimate the value of this theory for the description of the behavior of various substances and the prediction of their properties and the processes originating therewith.

SIMILARITY OF THE PROPERTIES OF LIQUID AND GASEOUS BODIES

The constriction of the law of corresponding states is due to the fact that it is based on the Van der Waals equation which does not possess sufficient generality. Mayer and independently Bogolyubov solved the problem of the equation of state of real gases; particular but nevertheless sufficiently effective approaches were developed simultaneously by Frenkel', Band, Vukalovich, and Novikov (see [2] for a brief survey). It became clear as a consequence of these papers that just as many individual constants associated with the nature of the substance enter the equation of state as are contained in the potential equation of molecular interaction, i.e., not less than three. And since the starting point for the formulation of the similarity conditions is the equations for the critical point $(\partial p/\partial v)_T = 0$, $(\partial^2 p/\partial v^2) = 0$, it is evident that by using these two equations it is impossible to express all the individual constants in terms of the pressure, temperature, and volume at the critical point: p_c , T_c , $v_c = 1/\rho_c$ and to reduce the equation of state to the dimensionless form in which parameters associated with the molecular structure would not be contained. Test showed, however, that it is possible to limit oneself to just one such structural parameter which is denoted by A^* by the Filippov assumption [3] (the dimensionless specific heat c_{p0}/R was taken

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as the parameter A^* in the ideal gas state, i.e., as $p \rightarrow 0$). An identical value of the parameter A^* for a number of substances denotes that they comprise a group of thermodynamically similar substances. Any thermodynamic quantity, including any macroscopic property, can be represented for them, as is shown in [1], in the form of an identical function of two out of the three parameters presented, for instance, $\pi = p/p_c$, $\vartheta = T/T_c$ and the parameter A^* . Kamerling-Onnes proposed expressing the viscosity as the product of powers of the critical parameters, the molecular weight μ , and the universal gas constant R_μ by a function of the presented parameters. The critical parameters are generalized molecular interaction characteristics, which makes such an expression quite general, referred to all the properties of substances. In other words, for thermodynamically similar substances any property Y can be represented in the form

$$Y = \mu^i p_c^j T_c^g R_\mu^l f_Y(p/p_c, T/T_c, A^*). \quad (1)$$

The values of i, j, g, l are $1/2, 2/3, -1/6, -1/6$ for viscosity, and according to [1], for heat conduction and the coefficient of self-diffusion they are, respectively, $-1/2, 2/3, -1/6, 5/6$ and $-1/2, -1/3, 5/6, 5/6$.

The generalized dependences (1) permit computation of the properties of gases and liquids, with a good degree of accuracy, by means of the known properties of their thermodynamic analogs. These dependences are the start for the prediction of the properties of liquid and gaseous substances, including for the search (prior to synthesis) for working substances with optimal properties.

Thermodynamic similarity considerations permit setting up an analogy later in the progress of processes of the same kind for the change in state of liquid and gaseous bodies, i.e., to simulate them [4]. This latter is quite important, in particular, for describing heat transfer in a moving liquid or gas medium: since the analytic solution of the equations of motion and heat transfer with the temperature dependence of the transfer coefficients taken into account is an extremely difficult problem, then in many cases it is preferable and fruitful to use thermodynamic similarity methods.

SIMILARITY OF PROPERTIES OF CRYSTALLINE SOLIDS

The extension of similarity considerations to the properties of crystalline bodies was delayed a long time by the ambiguity in the question of whether there is a special point for these bodies that would be the analog of the critical point so that its parameters could be the characteristic scales of the state. Definiteness was introduced by the theory of phase transitions of the second kind that is associated with the name of Landau.

Phase transitions in crystalline bodies are characterized by a change in the symmetry of the initial crystalline phase, where the high-temperature phase is usually, but not always, more symmetric. The symmetry is determined by the magnitude of a parameter of order η which is a quantitative estimate of the long-range order selected by a definite condition with respect to a certain physical property. In the more symmetric phase η is taken equal to zero; in the less symmetric phase η varies between 1 and 0 until reaching the phase transition point. For phase transitions of the second kind the order parameter varies continuously and for transitions of the first kind, in a jump from the value η' to 0 at the transition point.

According to Landau, the Gibbs energy density ϕ of the crystalline phase equals

$$\phi = \phi_0 + A\eta^2 + B\eta^4 + C\eta^6, \quad (2)$$

where ϕ_0, A, B, C are functions of p, T . The expression for ϕ refers to both the equilibrium and non-equilibrium states, where the conditions $d\phi = 0, d^2\phi > 0$ should be satisfied by virtue of the known thermodynamics theorem on the minimum Gibbs energy in the equilibrium state. Consequently, B and C will be positive in sign in the domain of phase transitions of the second kind, while A is positive in a more symmetric and negative in a less symmetric phase, i.e., vanishes at the transition point. The equality

$$A(p, T) = 0 \quad (3)$$

is the equation of the line of phase transitions of the second kind.

In the domain of phase transitions of the first kind the quantity B is negative. The point determined by the equations

$$A(p, T) = 0; B(p, T) = 0 \quad (4)$$

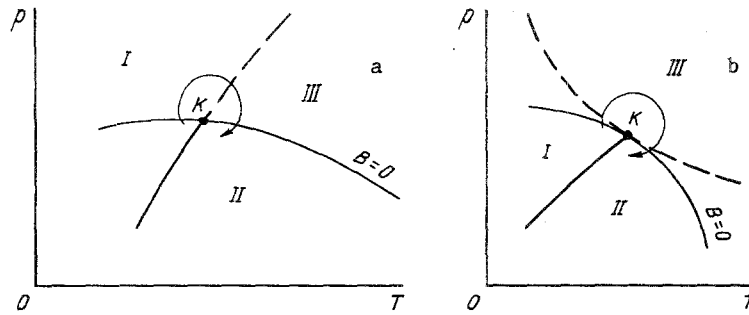


Fig. 1. Phase diagram of a crystal with a tricritical (a) and a bicritical (b) point.

is called the critical point of the crystal and its parameters are denoted by p_{cc} , T_{cc} .

The chemical potential ϕ/ρ of each of the phases is identical on the line of phase transitions. For phase transitions of the first kind the chemical potential of the more symmetric phase is $\phi_0^{(2)}/\rho^{(2)}$, while taking into account the jump in the order parameter from $\eta = \eta'$ to $\eta = 0$ in the less symmetric phase, it is $\phi_0^{(1)}/\rho^{(1)} + A(\eta - \eta')^2/\rho^{(1)} + B(\eta - \eta')^4/\rho^{(1)} + C(\eta - \eta')^6/\rho^{(1)}$. From the equality $\phi^{(2)}/\rho^{(2)} = \phi^{(1)}/\rho^{(1)}$ that should be satisfied both for $\eta = \eta'$ and $\eta = 0$, it follows that $-A\eta'^2 - B\eta'^4 - C\eta'^6 = 0$. This equation should result in one unique value of η' that will hold for $A > 0$ if

$$B^2 = 4AC. \quad (5)$$

Landau first obtained (5), although by a somewhat different means [5]; it determines the form of the line of phase transitions of the first kind near the critical point. The phase diagram corresponding to this case is shown in the figure a: the line of phase transitions of the first kind (solid curve) goes over continuously into the line of phase transitions of the second kind (dashed line) at the point K. The point K is called tricritical. Since (5) is satisfied only for $A > 0$, then evidently the boundary of the limits states of the more symmetric phase, i.e., its corresponding branch of spinodals, is characterized by $A = 0$.

For $A < 0$ the unique value of η' is determined by the positive root of the equation for η' , i.e., $\eta'^2 = -(1/2C)(B - \sqrt{B^2 - 4AC})$. The phase diagram for this case is displayed in the figure b; the phase III is more symmetric than the phases I and II. The line $B = 0$ is tangent to the line of phase transitions of the second kind at the point K while the line of phase transitions of the first kind is terminated at the point K that makes a certain angle with the line of phase transitions of the second kind; the point K is called bicritical.

The critical point of a crystal (tricritical or bicritical depending on the kind of phase diagram) plays the same role for anisotropic bodies as the ordinary critical point plays for isotropic bodies, i.e., liquid and gaseous bodies. This is at least clear from the fact that, as is shown in the figure, it is possible to go continuously over from the phase I to II in the domain of the critical point of the crystal K; at the point K itself all the phases are identical. Hence, the partial derivatives of ϕ with respect to η from second to fifth order hence vanish at the critical point of the crystal while, taking into account that the order parameter is the difference of the densities $\rho - \rho_c$ at the ordinary critical point in this case, the second and third of the mentioned derivatives equal zero to a lesser degree.

The parameters of the crystal critical point p_{cc} , T_{cc} can be taken as the characteristic scales of the crystalline state. Consequently, by analogy with (1) any property Y of the crystalline body can be represented in the form

$$Y = \mu^i p_{cc}^j T_{cc}^g R_{\mu}^l f_Y \left(\frac{p}{p_{cc}}, \frac{T}{T_{cc}}, A_c^* \right), \quad (6)$$

where A_c^* is a structural parameter associated with the relatively fine features of the crystal internal configuration while the function f_Y is identical for thermodynamically similar substances.

The similarity of the properties of crystalline bodies is manifest most clearly in the identical universal nature of the progress of phase transitions of the second kind in different substances. In direct proximity to the phase transition point T_c the properties vary according to the power law

$$Y = \text{const} |1 - T/T_c|^b, \quad (7)$$

where b is the so-called critical index inherent to this property. It is denoted in terms of β for the order parameter, for the susceptibility $1/(\partial^2 \phi / \partial \eta^2)$ in terms of $-\gamma$, for the r.m.s. fluctuations of order η^2 in terms of $-m'\nu$ (where m' takes on the values 0, 1, 2, ... [6]). Values of the critical indices are interrelated by definite relationships whose number is two and in certain cases three less than the number of the critical indices themselves. This means that the number of independent critical indices, and therefore, the number of individual constants associated with the nature of the substance also, does not exceed three for crystalline bodies. The above explains fully the similarity of processes of the change of state of crystalline bodies, including even the phase transitions of the second kind. A single definite set of values of the critical indices corresponds to the group of thermodynamically similar substances. In particular $\beta = 0.33$, $\gamma = 1.26$, $\nu = 0.64$ (for $m' = 0$) for bodies for which the phase transitions of the second kind are accompanied by strong fluctuations.

The values of p_{CC} , T_{CC} in (6) are unknown in practice for the majority of substances. This certainly reduces the role of (6), which should yet be considered as a formula not suitable for practical purposes but more often as an expression of the thermodynamic similarity of crystalline bodies. Moreover, the values of p_{CC} are apparently quite large, which can complicate their utilization. The question naturally occurs as to whether or not there are other scale characteristics for crystalline bodies that could be utilized in place of p_{CC} , T_{CC} . An exact answer is difficult; however, it can be assumed that such characteristics exist. Frenkel' [7] noted the important role of vacancies in the processes of the change of state of crystals. It is manifest in the fact that the order parameter can be expressed as the ratio between the difference in the numbers of sites occupied by atoms and the free (vacant) sites near some atom of the crystalline lattice and the number of occupied sites. Starting from this it is legitimate to assume that the quantity E/v_a , where v_a is the activation volume, which is equal in order of magnitude to the volume of a crystal elementary cell, can be considered as a certain characteristic pressure scale later denoted by p_B . As regards the temperature scale, it can be the temperature of the triple point T_{tr} ; let us recall that the melting point T_m at atmospheric pressure differs slightly from T_{tr} . A possible objection that since the liquid, gaseous and crystalline phases exist in equilibrium at the triple point, then the quantity T_{tr} turns out to be the characteristic scale not so much for the crystalline phase as for the other two, is removed by the fact of low pressure at the triple point. Consequently, the gas phase at the triple point can be considered an ideal gas and its presence will be equivalent to what would be if the condition of equality of its magnitude

$$\int c_p dT - T \int \frac{c_p}{T} dT + \text{const}$$

were imposed on the chemical potential of the crystalline phase. This condition is of so general a nature that it fully justifies the utilization of T_{tr} as the characteristic temperature scale. Therefore, p/p_B can apparently be taken in place of p/p_{CC} in (6) and the ratio T/T_{tr} or T/T_m in place of T/T_{CC} (here its value is referred to T_m by taking account of the weak temperature dependence of E). Comparison with test should show how allowable is such a modification of (6).

On the basis of (6) we have for the melting curve

$$p = p_B f(T/T_{tr}, A^*).$$

The melting curves of thermodynamically similar substances agree in the p/p_B , T/T_{tr} (or T/T_m) coordinates. It is pertinent to note that according to test data, the relative magnitudes of the differences in the volumes and entropies of the liquid and crystalline phases $(V_\mu^l - V_\mu^c)/V_\mu^c$, $(S_\mu^l - S_\mu^c)/S_\mu^c$ tend to constant values as the temperature rises on the section of the melting curve where $dp/dT > 0$, which denotes the constancy of dp/dT also at high temperatures.

SIMILARITY RELATIONSHIPS IN TRANSITION PROCESSES OF DISSIPATIVE STRUCTURES

The evolution of open thermodynamic systems is due to a change in the external conditions and consists in the rearrangement or replacement of the initial dissipative structure by another dissipative structure inherent to this system. This evolution is also called self-

organization. According to Prigogine [8], it can be considered as a sequence of phase transitions. This deduction is based on the analogy between the rearrangement of a dissipative structure and a phase transition of the second kind since the change in external conditions in both cases results in instability of the initial state and, consequently, the cooperative nature of the interaction of the enormous number of particles comprising the system, and in the formation of fluctuations of so large a scale that molecular singularities are not manifest here in practice; the formation of fluctuations denotes rupture of the original structure and the formation of a new one. Starting from this deduction in principle, the characteristic regularities (7) for phase transitions can be extended to the dissipative structure rearrangement process and the relations between the values of the dissipative fluxes in the original and newly formed structures are thereby clarified. The importance of such relations, especially taking their generality and universality into account, is obvious. It is illustrated well in the example of the transition of a laminar fluid flow into a turbulent one that is accompanied by a change in the heat transmission law (and conceivably, the resistivity). Since the laminar motion equations allow of exact solutions while such solutions are still unrealizable for turbulent motion, then by using the relationships (7) it is possible to find the value of the heat elimination coefficient in a turbulent flow for phase transitions by means of the exact solution for its value in a laminar flow. This possibility, which has an incomparably better foundation than the approximate approaches utilized up to now, opens new paths for the analysis of complex heat transfer problems (as well as of hydraulic resistance and mass transfer) under turbulent flow conditions. Because of the presence of a fluctuating velocity resulting in the growth of the effective value of the transport coefficients, a turbulently moving fluid should here be considered as the analog of a less symmetric, i.e., more ordered, phase and a laminarily moving fluid as a more symmetric phase.

In order to make clear the sequence of the analysis presented, we first consider the simplest problem of heat transfer between a flat plate and a turbulent fluid flow. As is known, the analytic solution for a laminar flow with $Pr = 1$ has the form $Nu = 0.67Re^{0.5}$. Since the difference $Nu/0.67 Re^{0.5} - 1$ equals zero for a laminar flow, then it can be considered the analog of the order parameter η . The number Re for whose critical value Re_{cr} laminar flow goes over into turbulent plays the same part as the temperature does for a phase transition. Using the equation $\eta = \text{const} |1 - T/T_c|^\beta$, where $\beta = 0.33$ and replacing η therein by $Nu/0.67 Re^{0.5} - 1$, and T by Re , we obtain

$$\frac{Nu}{0.67 Re^{0.5}} - 1 = \text{const} \left(\frac{Re}{Re_{cr}} - 1 \right)^\beta. \quad (8)$$

For $Re \gg Re_{cr}$ the one in the left side can be discarded, whereupon we have $Nu \sim Re^{0.5+\beta} = Re^{0.83}$, which is in good correspondence with test data according to which $Nu \sim Re^{0.8}$.

It can therefore be considered proved that the degree of the number Re in the expression for the number Nu , and therefore, for the heat elimination coefficient in a turbulent flow also, is 0.8 for large Re . As regards the degree of the number Pr (for $Pr \neq 1$), it is not determined here, particularly because the constant in the right side of the equation for the analog η can contain the number Pr . Because of its generality, (9) can even be applied for the transition domain $Re \geq Re_{cr}$. The problem of heat transfer during nucleate boiling of a liquid is more complex. The analytic solution for the case when the free convective motion of the boiling liquid is laminar is mentioned in [9], by starting from equally likely but still approximate assumptions and the case of turbulent convective motion of a boiling fluid was also examined. It turns out that the expressions for the heat flux density q can be written in a single manner in both cases

$$\frac{q (c_p \rho)^2}{\alpha \rho^2 r Pr^{1/4}} \sqrt{\frac{2\sigma\alpha}{\Delta p}} \sqrt{\frac{\rho}{\Delta p}} = \text{const} Pr^m Re^n, \quad (9)$$

where m, n are $1/3, 1/2$ for laminar motion and $-1/4, 0.8$ for turbulent. The number $Re = a/\nu da/d\tau$ is expressed in terms of the radius a of a vapor bubble averaged with respect to time; $\Delta p = r(T_h - T_s)/T_s$; T_h is the liquid temperature at the heating surface, where $T_h - T_s = 2\sigma T_s/\rho''ra$.

If $\Delta p, T_h - T_s$ in (9) are expressed in terms of a , then the heat elimination coefficient α (taking into account that the quantity $a da/d\tau$ grows weakly with a) will be proportional to the radius of the vapor bubble a to a power somewhat greater than 0.25 for turbulent convective motion of the boiling liquid, where the bubble radius itself equals the dimension, in

order of magnitude, of the heating surface indentation in which the bubbles are formed.

In order to see the correctness of (9) for turbulent free convective motion of a boiling liquid, we will start from the exact solution for the case of laminar free convective motion of a boiling liquid. It is easy to see that the role of the order parameter in the case under consideration is played by the difference in the ratio between the right side of (9) for the laminar mode and its left side and one. On the basis of the general expression (7) for η , we conclude that for $Re \gg Re_{cr}$ this ratio will be proportional to $Re^{0.33}$, from which there results that the degree of the number Re in (9) will indeed equal 0.8 in the case of turbulent convective motion of a boiling liquid.

Shekriladze [10] thoroughly analyzed (9) for nucleate boiling of a fluid in turbulent free convective motion and arrived at the following conclusion: a) equation (9) agrees with test data and is identical to the equation proposed later by Shekriladze and his colleagues: $Nu = 1.22 \cdot 10^{-2} \cdot K^{0.7} Re^{*0.25}$, $K = qa^2 r \rho'' / \sigma \lambda T_s$, $Re^* = \sqrt{p(v'' - v) 2 T_s \rho c_p / \nu \rho''^2 r^2}$; b) the theory of nucleate boiling developed in [9] has a physical foundation and permits clarification of the means for intensification of this kind of heat transfer for small thermal drops; c) the deduction resulting from (9) about the increase in the heat elimination coefficient as the vapor bubble size grows is of value in principle, since the fact that approximately five years after the publication of [9] porous surfaces capable of forming vapor bubbles of comparatively large size were proposed for the intensification of heat transfer during boiling must be referred back to c).

NOTATION

T , absolute temperature, °K; p , pressure; v , specific volume; ρ , density; μ , molecular mass; R , gas constant; T_C , p_C , v_C , critical point parameters; T_{CC} , p_{CC} , v_{CC} , crystal tricritical or bicritical point parameters; T_{tr} , triple point temperature; T_m , melting point at atmospheric pressure; E , energy of vacancy formation; v_a , activation volume; p_B , ratio E/v_a ; ϕ , Gibbs energy density; η , order parameter; T_C , a point of a phase transition of the second kind; $1/(d^2\phi/d\eta^2)$, susceptibility; α , β , γ , ν , critical exponents; c_p , specific heat for $p = \text{const}$; ν_B , kinematic viscosity; κ , fluid thermal conductivity; λ , heat conduction; r , heat of vapor formation; σ , surface tension; ρ'' , saturated vapor density; T_h , fluid heating temperature; T_s , saturation temperature; q , thermal flux density; α_T , coefficient of heat elimination; a , vapor bubble radius; τ , time; Re , Reynolds number; Pr , Prandtl number; Nu , Nusselt number.

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